From alkynes to carbenes mediated by [Re(Br)(H)(NO)(PR3)2] (R = Cy, iPr) complexes

Jiang, Y ; Blacque, O ; Fox, T ; Frech, C M ; Berke, H

Abstract: Five-coordinate rhenium(I) hydride complexes of the type [Re(Br)(H)(NO)(PR3)2] (R = Cy 1a, iPr 1b) were reacted with terminal alkynes R1C CH (R1 = Ph, SiEt3, H), yielding 18-electron 2-alkyne adducts [Re(Br)(H)(NO)(PR3)2(2-HC CR1)] (R1 = Ph (R = Cy 2a, iPr 2b), SiEt3 (R = Cy 4a, iPr 4b), H (R = Cy 6a, iPr 6b)). Alkyne insertion into the Re−H bond led to the formation of rhenium(I) 1-vinyl derivatives [Re(Br)((E)-CH CHR1)(NO)(PR3)2] (R1 = Ph (R = Cy 3a, iPr 3b), SiEt3 (R = Cy 5a, iPr 5b), H (R = Cy 7a, iPr 7b)) in good yields. The rate of formation of the vinyl complexes depends on R1 in the order SiEt3 > Ph > H, and the reactions of 1b bearing the PiPr3 ligand are generally faster than those of 1a with PCy3. 1a,b were also reacted with 2-methyl-1-buten-3-yne and 1,7-octadiyne, affording dienyl derivatives [Re(Br)(E)-CH CHC(CH3) CH2(NO)(PR3)2] (R = Cy 8a, iPr 8b) and the binuclear -bis-alkenyl compounds [(PR3)2(NO)(Br)Re(E)-CH CH-(CH2)4-CH CH-(E)Re(Br)(NO)(PR3)2] (R = Cy 9a, iPr 9b). The reactions of 3a,b or 5a,b with HBF4 · OEt2 afforded the rhenium(I) carbene derivatives [Re(F)(Br)(CHCH2Ph)(NO)(PR3)2] (R = Cy 10a, iPr 10b) or [Re(F)(Br)(CHCH C(CH3)2)(NO)(PR3)2] (R = Cy 11a, iPr 11b) via protonation at the - and - carbon of the vinyl group, respectively. The fluorine ligands are located cis to the carbene ligand and the bromo atom cis to the nitrosyl group. The binuclear species 9a,b were also reacted with HBF4 · OEt2 to afford the binuclear carbene derivatives [(PR3)2(NO)(Br)(F)Re CH-(CH2)6-CH Re(F)(Br)(NO)(PR3)2] (R = Cy 12a, iPr 12b). The molecular structures of 3a, 5a, and 11a were established by X-ray diffraction studies.

DOI: https://doi.org/10.1021/om900459x

4670 *Organometallics* **2009,** *28,* 4670–4680
DOI: 10.1021/om900459x

ORGANOMETALLICS
Article

From Alkynes to Carbenes Mediated by [Re(Br)(H)(NO)(PR_3)$_2$] (R = Cy, *i*Pr) Complexes

Yanfeng Jiang, Olivier Blacque, Thomas Fox, Christian M. Frech, and Heinz Berke*

Anorganisch-Chemisches Institut, Universität Zürich, Winterthurerstrasse 190, CH-8037, Zürich, Switzerland

Received May 29, 2009

Five-coordinate rhenium(I) hydride complexes of the type [Re(Br)(H)(NO)(PR_3)$_2$] (R = Cy **1a**, *i*Pr **1b**) were reacted with terminal alkynes $R^1C{\equiv}CH$ (R^1 = Ph, $SiEt_3$, H), yielding 18-electron η^2-alkyne adducts [Re(Br)(H)(NO)(PR_3)$_2$(η^2-$HC{\equiv}CR^1$)] (R^1 = Ph (R = Cy **2a**, *i*Pr **2b**), $SiEt_3$ (R = Cy **4a**, *i*Pr **4b**), H (R = Cy **6a**, *i*Pr **6b**)). Alkyne insertion into the Re−H bond led to the formation of rhenium(I) η^1-vinyl derivatives [Re(Br)((*E*)-$CH{=}CHR^1$)(NO)(PR_3)$_2$] (R^1 = Ph (R = Cy **3a**, *i*Pr **3b**), $SiEt_3$ (R = Cy **5a**, *i*Pr **5b**), H (R = Cy **7a**, *i*Pr **7b**)) in good yields. The rate of formation of the vinyl complexes depends on R^1 in the order $SiEt_3$ > Ph > H, and the reactions of **1b** bearing the P*i*Pr$_3$ ligand are generally faster than those of **1a** with PCy_3. **1a**,**b** were also reacted with 2-methyl-1-buten-3-yne and 1,7-octadiyne, affording dienyl derivatives [Re(Br){(*E*)-$CH{=}CHC(CH_3){=}CH_2$}(NO)(PR_3)$_2$] (R = Cy **8a**, *i*Pr **8b**) and the binuclear μ-bis-alkenyl compounds [(PR_3)$_2$(NO)(Br)Re{(*E*)-$CH{=}CH$-$(CH_2)_4$-$CH{=}CH$-(*E*)}Re(Br)(NO)(PR_3)$_2$] (R = Cy **9a**, *i*Pr **9b**). The reactions of **3a**,**b** or **5a**,**b** with $HBF_4{\cdot}OEt_2$ afforded the rhenium(I) carbene derivatives [Re(F)(Br)($=CHCH_2Ph$)(NO)(PR_3)$_2$] (R = Cy **10a**, *i*Pr **10b**) or [Re(F)(Br)($=CHCH{=}C(CH_3)_2$)(NO)(PR_3)$_2$] (R = Cy **11a**, *i*Pr **11b**) via protonation at the β- and δ-carbon of the vinyl group, respectively. The fluorine ligands are located *cis* to the carbene ligand and the bromo atom *cis* to the nitrosyl group. The binuclear species **9a**,**b** were also reacted with $HBF_4{\cdot}OEt_2$ to afford the binuclear carbene derivatives [(PR_3)$_2$-(NO)(Br)(F)Re{$=CH$-$(CH_2)_6$-$CH{=}$}Re(F)(Br)(NO)(PR_3)$_2$] (R = Cy **12a**, *i*Pr **12b**). The molecular structures of **3a**, **5a**, and **11a** were established by X-ray diffraction studies.

Introduction

Transition metal hydrides undergo a wide variety of reactions, which are of synthetic and catalytic significance.[1,2] In this regard the d^6 square-pyramidal hydride complexes [M(X)(H)(CO)(PR_3)$_2$] (M = Ru, Os, X = halide)[3] are appropriate examples, since they display rich organometallic chemistry[4] and are versatile catalysts.[5] One of their typical reaction modes is the insertion of terminal alkynes into their M−H bonds, producing vinyl derivatives.[6] Mechanistic studies indicated the formation of six-coordinate η^2-alkyne adducts as initial intermediates, which however were unstable and could be observed only in special cases via *in situ* low-temperature NMR.[7] Furthermore, the β-carbon of the vinyl group displays marked nucleophilic character due to a significant contribution of the zwitterionic resonance form of transition metal vinyl moieties. As a result, carbene derivatives were expected to be accessible

*Corresponding author. E-mail: hberke@aci.uzh.ch.

(1) (a) Peruzzini, M; Poli, R. In *Recent Advances in Hydride Chemistry*; Elsevier: Amsterdam, Holland, 2001. (b) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; Wiley-Interscience, 2001.

(2) (a) Ito, M; Ikariya, T. *Chem. Commun.* **2007**, 5134. (b) Esteruelas, M. A.; Oro, L. A. *Chem. Rev.* **1998**, *98*, 577.

(3) (a) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221. (b) Esteruelas, M. A.; Oro, L. *Adv. Organomet. Chem.* **2001**, *47*, 1.

(4) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Meyer, U.; Werner, H. *Angew. Chem., Int. Ed.* **1988**, *27*, 1563. (b) Lay, P. A.; Harman, W. D. *Adv. Inorg. Chem.* **1991**, *37*, 219. (c) Albeniz, M. J.; Buil, M. L.; Esteruelas, M. A.; Lopez, A. M.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 3746. (d) Bakhmutov, V. I.; Bertran, J.; Esteruelas, M. A.; Lledos, A.; Maseras, F.; Modrego, J.; Oro, L. A.; Sola, E. *Chem.—Eur. J.* **1996**, *2*, 815. (e) Esteruelas, M. A.; Gomez, A. V.; Lahoz, F. J.; Lopez, A. M.; Onate, E.; Oro, L. A. *Organometallics* **1996**, *15*, 3423. (f) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Onate, E.; Peinado, E.; Ruiz, N. *Organometallics* **1997**, *16*, 5748. (g) Yi, C. S.; Lee, D. W. *Organometallics* **1999**, *18*, 5152. (h) Rowley, C. N.; Foucault, H. M.; Woo, T. K.; Fogg, D. E. *Organometallics* **2008**, *27*, 1661.

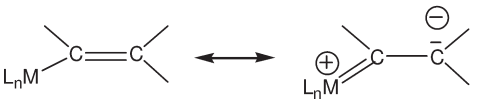
(5) (a) Esteruelas, M. A.; Sola, E.; Oro, L. A.; Werner, H.; Meyer, U. *J. Mol. Catal.* **1988**, *45*, 1. (b) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1991**, *10*, 462. (c) Parent, J. S.; McManus, N. T.; Rempel, G. L.; Power, W. P.; Marder, T. B. *J. Mol. Catal. A: Chem.* **1998**, *135*, 285. (d) Esteruelas, M. A.; Herrero, J.; Lopez, A. M.; Olivan, M. *Organometallics* **2001**, *20*, 3202. (e) Cobo, N.; Esteruelas, M. A.; Gonzalez, F.; Herrero, J.; Lopez, A. M.; Lucio, P.; Olivan, M. *J. Catal.* **2004**, *223*, 319. (f) Sanchez, R. P.; Connell, B. T. *Organometallics* **2008**, *27*, 2902.

(6) (a) Werner, H.; Esteruelas, M. A.; Otto, H. *Organometallics* **1986**, *5*, 2295. (b) Andriollo, A.; Esteruelas, M. A.; Meyer, U.; Oro, L. A.; Sanchez-Delgado, R. A.; Sola, E.; Valero, C.; Werner, H. *J. Am. Chem. Soc.* **1989**, *111*, 7431. (c) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Zeier, B. *Organometallics* **1994**, *13*, 1662. (d) Esteruelas, M. A.; Oro, L. A.; Valero, C. *Organometallics* **1995**, *14*, 3596. (e) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Sola, E. *J. Am. Chem. Soc.* **1996**, *118*, 89. (f) Buil, M. L.; Esteruelas, M. A. *Organometallics* **1999**, *18*, 1798. (g) Esteruelas, M. A.; Lopez, A. M.; Onate, E. *Organometallics* **2007**, *26*, 3260.

(7) (a) Marchenko, A. V.; Gerard, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 1244. (b) Marchenko, A. V.; Gerrad, H.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2001**, *25*, 1382.

 Published on Web 07/28/2009

via protonation or a trapping with other electrophiles at the β-carbon atom.[8,4b,4c]

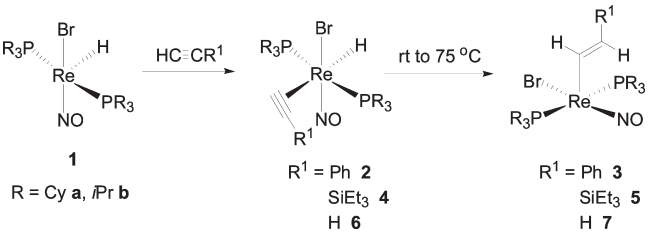


In recent years our group focused on the exploration of a hydride chemistry of the middle transition metal centers,[9] in particular with respect to the development of polar homogeneous catalyses involving H−H, H−Si, and H−B activations.[10] In the realm of complexes with rhenium centers a special type of five-coordinate, 16-electron rhenium(I) hydride species $[Re(Br)(H)(NO)(PR_3)_2]$ (R = Cy **1a**, *i*Pr **1b**) was discovered accessible from rhenium(I) dihydrogen complexes.[11] Such mononitrosyl Re(I) hydride complexes of type **1** are isoelectronic to the mentioned monocarbonyl Ru(II) or Os(II) hydrides and resemble these structurally to a great extent. The chemistry of these rhenium hydrides comprised reactions that allowed access to a variety of mono-, di-, and tetrahydride species.[12] In extension of this work, we report here their transformations with terminal alkynes apparently occurring in a stepwise manner to form rhenium(I) vinyl compounds, which may then be reacted further with proton sources to yield carbene derivatives.

Results and Discussion

Insertion of Terminal Alkynes into the Re−H Bond of $[Re(Br)(H)(NO)(PR_3)_2]$ Complexes (R = Cy 1a, *i*Pr 1b). Treatment of the violet solutions of the complexes $[Re(Br)(H)(NO)(PR_3)_2]$ (R = Cy **1a**, *i*Pr **1b**) in benzene-d_6 with phenylacetylene afforded at room temperature immediately a light yellow solution with quantitative formation of the phenylacetylene-coordinated rhenium(I) hydride adducts $[Re(Br)(H)(NO)(PR_3)_2(\eta^2\text{-}HC{\equiv}CPh)]$ (R = Cy **2a**, *i*Pr **2b**). Both compounds **2a** and **2b** were isolated as light yellow solids in 90% and 85% yields. The $^{31}P\{^1H\}$ NMR spectra of **2a** displayed signals with AB patterns at δ 13.9 and 11.4 ppm ($^2J_{(PP)}$ = 122 Hz), indicating chemically inequivalent *trans* phosphorus ligands. This observation contrasts the appearance of only one singlet signal at 20.8 ppm for **2b**, suggesting equivalent *trans* phosphorus positions and free rotation of the acetylene ligand around the Re(acetylene) bond in the less sterically hindering P*i*Pr$_3$ environment. In the ^1H NMR spectra of both complexes the hydride signals were observed as triplets at δ 5.32 ppm (**2a**) and 4.90 ppm (**2b**), which were strongly shifted low-field in comparison with the related signals of **1a** (−17.6 ppm) or **1b** (−16.7 ppm). This pronounced effect was rationalized on the basis of strong d-electron back-donation from the rhenium center to the π^* orbital of the η^2-alkyne, which apparently caused a substantial decrease of the electron density at the *trans* hydride site. Thus the coordinated alkyne acts as a strong π acceptor, most probably oriented parallel to the P−Re−P axis, in compliance with the previously reported structures of the η^2-styrene adducts $[Re(Br)(H)(NO)(PR_3)_2(\eta^2\text{-}CH_2{=}CHC_6H_4\text{-}(p\text{-}CH_3))]$.[11] The terminal protons of phenylacetylene gave rise to a doublet or a multiplet signal at δ 8.82 (d) for **2a** and at 8.78 (m) ppm for **2b**, respectively.

Scheme 1



Complexes **2a** and **2b** are stable in the solid state. In solution at room temperature, their light yellow color turns green within approximately 15 h. Upon heating to 75 °C for 0.5−3 h, the solutions turned a deeper green, indicating chemical changes. NMR spectroscopy provided evidence for complete formation of the rhenium(I) vinyl complexes of type $[Re(Br)((Z)\text{-}CH{=}CHPh)(NO)(PR_3)_2]$ (R = Cy **3a**, *i*Pr **3b**), which were isolated as deep green powders in 95% and 90% yield (Scheme 1). Complexes **3a** and **3b** were both fully characterized by elemental analysis, IR, and ^1H, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ NMR spectroscopy. The IR spectra of **3a** or **3b** showed a strong ν(NO) absorption at 1648 (**3a**) or 1643 cm^{-1} (**3b**) at low wavenumbers, indicating electron-rich rhenium centers. The $^{31}P\{^1H\}$ NMR spectra displayed a singlet at δ 14.2 (**3a**) or 29.8 ppm (**3b**) in accord with the *trans* disposition of the phosphine ligands. In the ^1H NMR spectra, the Re-CH=CH− vinyl protons were observed as doublets at δ 9.47, 5.50 ppm (**3a**, $^3J_{(HH)}$ = 13.0 Hz) and 9.21, 5.46 ppm (**3b**, $^3J_{(HH)}$ = 13.0 Hz), respectively. The magnitude of the $J_{(HH)}$ coupling constants suggests an *E*-stereochemistry of the −CH=CH− double bond.[13] The presence of vinyl ligands was supported further by the $^{13}C\{^1H\}$ NMR spectra, which displayed resonances of the $C_\alpha(sp^2)$ and $C_\beta(sp^2)$ carbon atoms at δ 151.3, 123.4 (**3a**) and 151.1, 123.5 ppm (**3b**). These data are comparable to those of the structurally analogous osmium or ruthenium vinyl compounds.[6]

Similarly, treatment of **1a** or **1b** with other terminal alkynes, such as (triethylsilyl)acetylene, led to initial formation of the acetylene adduct $[Re(Br)(H)(NO)(PR_3)_2(\eta^2\text{-}HC{\equiv}CSiEt_3)]$ (R = Cy **4a**, *i*Pr **4b**). In the ^{31}P NMR spectra characteristic AB patterns were found at 16.1 and 13.7 ppm for **4a** ($^2J_{(PP)}$ = 112 Hz) and at 26.3 and 18.5 ppm ($^2J_{(PP)}$ = 121 Hz) for **4b**, suggesting a preferred orientation of the acetylene ligand in the P−Re−P axis, hindered rotation around the Re−acetylene bond, and a considerable binding strength of

(8) (a) Esteruelas, M. A.; Lopez, A. M.; Olivan, M. *Coord. Chem. Rev.* **2007**, *251*, 795. (b) Esteruelas, M. A.; Lahoz, F. J.; Onate, E.; Oro, L. A.; Valero, C.; Zeier, B. *J. Am. Chem. Soc.* **1995**, *117*, 7935.

(9) (a) Choualeb, A.; Blacque, O.; Schmalle, H. W.; Fox, T.; Hiltebrand, T.; Berke, H. *Eur. J. Inorg. Chem.* **2007**, 5246. (b) Frech, C. M.; Blacque, O.; Schmalle, H. W.; Berke, H.; Adlhart, C.; Chen, P. *Chem.—Eur. J.* **2006**, *12*, 3325. (c) Frech, C. M.; Blacque, O.; Schmalle, H. W.; Berke, H. *Chem.—Eur. J.* **2006**, *12*, 5199. (d) Kurz, P.; Rattat, D.; Angst, D.; Schmalle, H.; Spingler, B.; Alberto, R.; Berke, H.; Beck, W. *Dalton Trans.* **2005**, 804. (e) Jaunky, P.; Schmalle, H. W.; Blacque, O.; Fox, T.; Berke, H. *J. Organomet. Chem.* **2005**, *690*, 1429. (f) Liu, X. Y.; Venkatesan, K.; Schmalle, H. W.; Berke, H. *Organometallics* **2004**, *23*, 3153. (g) Messmer, A.; Jacobsen, H.; Berke, H. *Chem.—Eur. J.* **1999**, *5*, 3341.

(10) (a) Choualeb, A.; Maccaroni, E.; Blacque, O.; Schmalle, H. W.; Berke, H. *Organometallics* **2008**, *27*, 3474. (b) Llamazares, A.; Schmalle, H. W.; Berke, H. *Organometallics* **2001**, *20*, 5277. (c) Gusev, D.; Llamazares, A.; Artus, G.; Jacobsen, H.; Berke, H. *Organometallics* **1999**, *18*, 75. (d) Jiang, Y.; Berke, H. *Chem. Commun.* **2007**, 3571.

(11) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Chem.—Eur. J.* **2009**, *15*, 2121.

(12) Jiang, Y.; Blacque, O.; Fox, T.; Frech, C. M.; Berke, H. *Organometallics*, submitted.

(13) (a) Mann, B. E.; Shaw, B. L.; Tucker, N. I. *J. Chem. Soc. A.* **1971**, *16*, 2667. (b) Clayden, J. *Organic Chemistry*; Oxford, 2000.

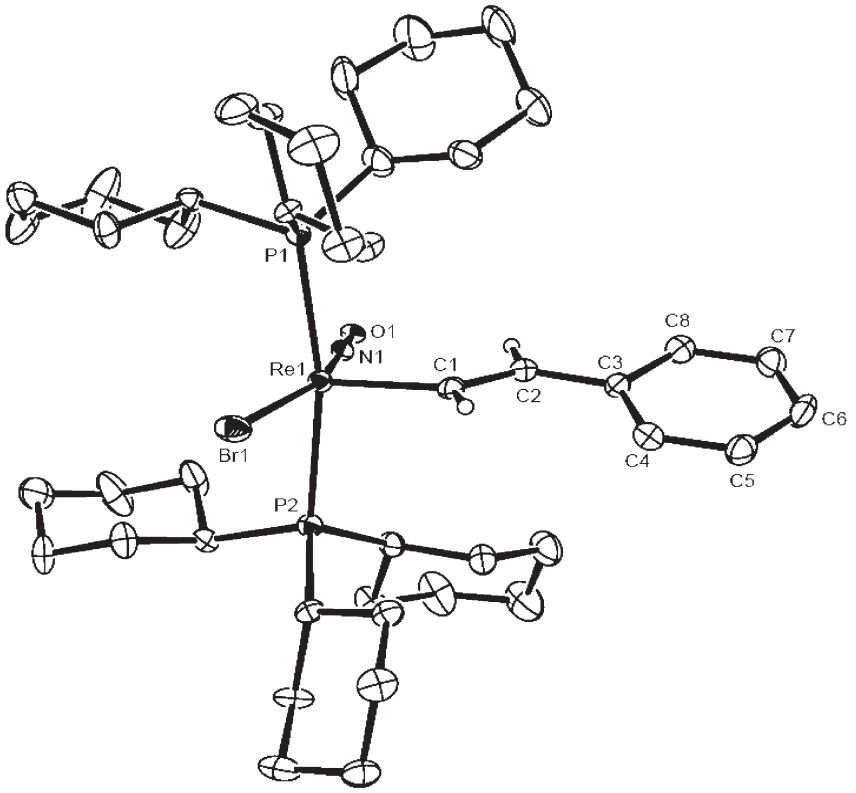


Figure 1. ORTEP drawing of [Re(Br)((*Z*)-CH=CHPh)(NO)(PCy_3)$_2$] (**3a**) with 30% probability ellipsoids. Selected bond lengths (Å): C(1)−Re(1), 2.020(4); C(1)−C(2), 1.372(7); N(1)−O(1), 1.085(6); N(1)−Re(1), 1.783(6); P(1)−Re(1), 2.4518(13); P(2)−Re(1), 2.4633(14); Br(1)−Re(1), 2.5389(6). Selected bond angles (deg): C(2)−C(1)−Re(1), 130.9(4); N(1)−Re(1)−C(1), 92.9(2); N(1)−Re(1)−P(1), 91.08(13); C(1)−Re(1)−P(1), 96.0(2); N(1)−Re(1)−P(2), 90.40(13); C(1)−Re(1)−P(2), 105.49(16); P(1)−Re(1)−P(2), 168.82(5); N(1)−Re(1)−Br(1), 161.53(14); O(1)−N(1)−Re(1), 177.5(4).

the acetylene. Within 5 min the light yellow solutions of **4a**,**b** rapidly turned green with formation of the vinyl complexes [Re(Br)((*Z*)-CH=CHSiEt_3)(NO)(PR_3)$_2$] (R = Cy **5a**, *i*Pr **5b**) in spectroscopic yields higher than 10%. After standing at room temperature for 10 h, full conversions were achieved in both cases. Isolation of **5a** and **5b** was accomplished in 62% and 59% yield, respectively. The increased reactivity in comparison with the phenylacetylene derivatives indicated facilitated hydride transfers from the rhenium center to the C_β atom of the terminal alkyne. This contrasts with the case of the related osmium hydride, where (trimethylsilyl)acetylene reacts slower than phenylacetylene, rationalized on the basis of the stronger electron-withdrawing ability of the Me_3Si group and increasing electrophilicity at C_β.[7a] The opposite effect was seen with the rhenium hydride complexes, explained here on the basis of predominant steric influences of the bulkier Et_3Si group, which causes thermodynamic preference for the vinyl complex with less steric congestion. The IR spectra of **5a** or **5b** showed strong ν(NO) absorption at 1648 (**5a**) and 1642 cm^{-1} (**5b**). The $^{31}P\{^1H\}$ NMR spectra displayed a singlet at δ 13.4 (**5a**) or 24.6 ppm (**5b**). In the ^1H NMR spectra, the signals of the Re-CH=CH− moiety were observed as doublets at δ 9.25, 4.92 (**5a**, $^3J_{(HH)}$ = 14.0 Hz) and 8.95, 4.89 ppm (**5b**, $^3J_{(HH)}$ = 14.0 Hz), indicating *E*-stereochemistry at the vinyl moiety. In the $^{13}C\{^1H\}$ NMR spectra, the $C_\alpha(sp^2)$ and $C_\beta(sp^2)$ carbon atoms are seen as singlets at δ 169.5, 125.8 (**5a**) and 170.2, 126.9 ppm (**5b**).

The molecular structures of **3a** and **5a** were established by single-crystal X-ray diffraction studies, as depicted in Figures 1[14] and 2.[15] Both complexes adopt a square-pyramidal geometry around the rhenium centers with the vinyl ligand occupying apical positions. The two phosphine ligands are bent toward the vacant site with P(1)−Re(1)−P(2) angles of 168.82(5)° for **3a** and 165.53(2)° for **5a**. Such a bending may originate from steric repulsion between the PCy_3 and the vinyl group but may also be driven by the C−H agostic interaction of the of PCy_3 ligand with the vacant site of the rhenium center. The NO group and the bromide are bending over to the vacant site with a N(1)−Re(1)−Br(1) angle of 161.53(14)° for **3a** and 164.56(8)° for **5a**. From the X-ray structure it became particularly evident that the phenyl group (or the triethylsilyl group) and the Re center are in *E*-positions, indicating a *syn* insertion pathway of the alkyne into Re−H bond. The C(1)−C(2) distances are in the typical range of C=C double bonds of 1.372(7) Å in **3a** and 1.337(4) Å

(14) X-ray crystal-structure data for **3a** (CCDC-730153): purple crystals, $C_{44}H_{73}BrNOP_2Re$, M = 960.08, crystal size 0.36 × 0.17 × 0.06 mm^3, orthorhombic, space group *Pna*21: a = 20.2785(3) Å, b = 10.1861(1) Å, c = 21.0659(3) Å, α = 90°, β = 90°, γ = 90°, V = 4351.35(10) $Å^3$, Z = 4, ρ_{calcd} = 1.466 $Mg\cdot m^{-3}$, $F(000)$ = 1968, μ = 3.817 mm^{-1}, 23 682 reflections ($2\theta_{max}$ = 56°), 10 030 unique (R_{int} = 0.0396), 452 parameters, $R_1(I > 2(I))$ = 0.0324, wR_2(all data) = 0.0679, GooF = 0.928, largest difference peak and hole 0.797 and −0.837 $e\cdot Å^{-3}$.

(15) X-ray crystal-structure data for **5a** (CCDC-730154): green crystals, $C_{44}H_{83}BrNOP_2ReSi$, M = 998.25, crystal size 0.28 × 0.17 × 0.11 mm^3, triclinic, space group $P\bar{1}$: a = 12.7359(1) Å, b = 12.8512(2) Å, c = 16.2393(2) Å, α = 69.673(1)°, β = 88.298(1)°, γ = 70.411(1)°, V = 2336.79(6) $Å^3$, Z = 2, ρ_{calcd} = 1.419 $Mg\cdot m^{-3}$, $F(000)$ = 1032, μ = 3.581 mm^{-1}, 58 570 reflections ($2\theta_{max}$ = 65°), 17 017 unique (R_{int} = 0.0287), 461 parameters, $R_1(I > 2(I))$ = 0.0294, wR_2(all data) = 0.0766, GooF = 1.042, largest difference peak and hole 1.676 and −1.728 $e\cdot Å^{-3}$.

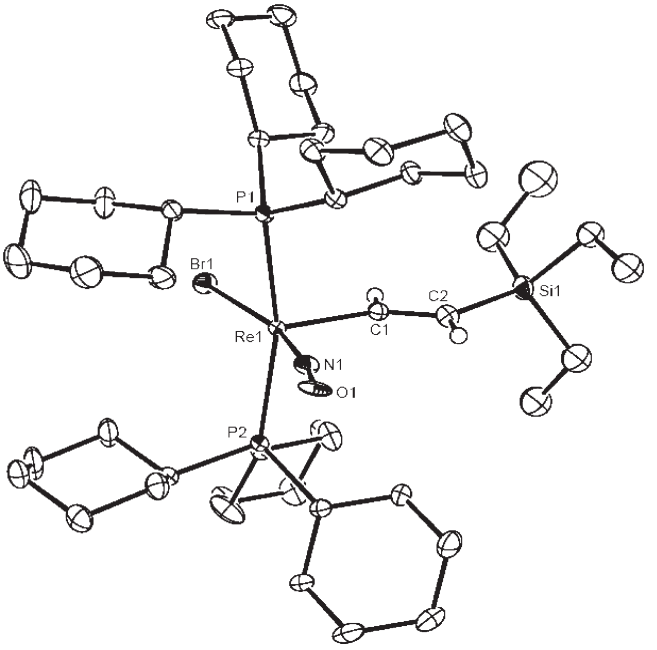


Figure 2. ORTEP drawing of [Re(Br)((*Z*)-CH=CHSiEt$_3$)(NO)(PCy$_3$)$_2$] (**5a**) with 30% probability ellipsoids. Selected bond lengths (Å): C(1)−Re(1), 2.021(2); N(1)−O(1), 1.080(3); N(1)−Re(1), 1.761(2); P(1)−Re(1), 2.4616(6); P(2)−Re(1), 2.4632(6); Br(1)−Re(1), 2.5501(3); C(1)−C(2), 1.337(4). Selected bond angles (deg): C(2)−C(1)−Re(1), 139.5(2); N(1)−Re(1)−C(1), 94.80(11); N(1)−Re(1)−P(1), 89.17(7); C(1)−Re(1)−P(1), 95.38(7); N(1)−Re(1)−P(2), 88.82(7); C(1)−Re(1)−P(2), 99.06(7); P(1)−Re(1)−P(2), 165.53(2); N(1)−Re(1)−Br(1), 164.56(8); O(1)−N(1)−Re(1), 170.2(2).

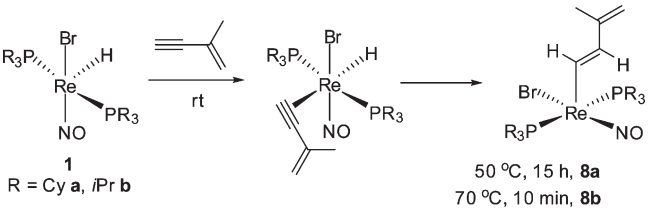
in **5a**.[16] The C(1)−C(2) distance of **3a** is longer than that of **5a**, which may originate from π conjugation with the neighboring almost in-plane phenyl group.

Previously we reported the preparation of acetylene-coordinated rhenium(I) hydride complexes [Re(Br)(H)(NO)(PR$_3$)$_2$(η^2-HC≡CH)] (R = Cy **6a**, *i*Pr **6b**), which in comparison with the above terminal η^2-alkyne adducts are rather stable at room temperature even for a longer period of time (7 days). However, at higher temperatures (75 °C) they slowly convert into the acetylene-inserted complexes [Re(Br)((*Z*)-CH=CH$_2$)(NO)(PR$_3$)$_2$] (R = Cy **7a**, *i*Pr 7**b**). The reaction of **6a** is rather sluggish, with a reaction time of 63 h to achieve 56% conversion along with two other unidentified organometallic species formed. **7a** could only be characterized *in situ* in solution, since attempts to isolate pure **7a** failed. In contrast, the reaction of **6b** is much faster, with a conversion rate of 92% at 75 °C within 15 h. The appearance of a deep blue color was accompanied by the appearance of a small amount of liberated P*i*Pr$_3$. Comparing the reactions of phenyl and triethylsilyl acetylene, the slower conversion of the η^2-acetylene adducts **6a**,**b** to form the vinyl compounds **7a**,**b** might provide additional evidence for steric influence on the alkyne insertion into the Re−H bond.

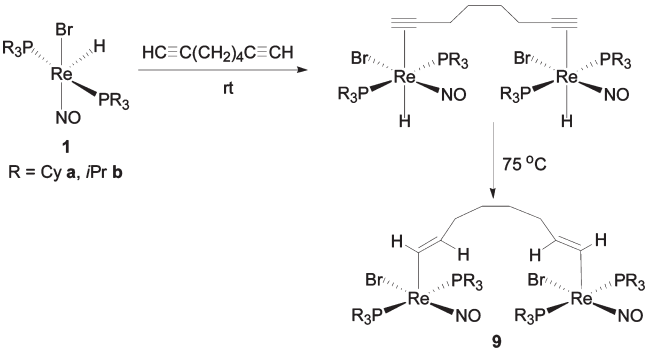
The IR spectra of **7b** displayed a strong ν(NO) absorption at 1664 cm^{-1}. The ν(NO) absorption of **7a** could not be extracted from the reaction mixture. The ^{31}P{^{1}H} NMR spectra showed singlets at δ 11.8 (**7a**) and 22.6 ppm (**7b**). In the ^{1}H NMR spectra the vinyl protons gave rise to signals at δ 8.60 (dd), 5.47 (d), 4.30 (d) ppm for **7a** and 8.30 (t), 5.46 (br), 4.27 (br) ppm for **7b**. In the ^{13}C{^{1}H} NMR spectra two resonances at δ 151.7, 115.5 ppm were assigned to the C$_\alpha$(sp^2) and C$_\beta$(sp^2) atoms of **7a**, and at 151.0, 116.3 ppm for **7b**. **7b** also gave a satisfactory elemental analysis.

(16) Bartell, L. S.; Roth, E. A.; Hollowel, C.; Kuchitsu, K.; Young, J. E. *J. Chem. Phys.* **1965**, *42*, 2683.

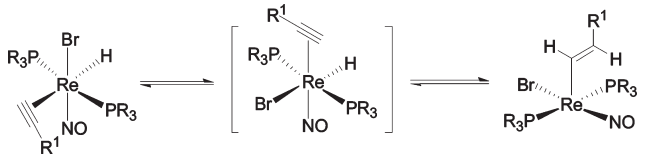
Scheme 2



Scheme 3



Scheme 4



In the presence of enynes, such as 2-methyl-1-buten-3-yne, selective coordination and subsequent reaction occurs for the C≡C triple bond (Scheme 2). The formed acetylene-coordinated complexes are thermodynamically unstable in solution and are gradually converted into their dienyl isomers [Re(Br){CH=CHC(CH$_3$)=CH$_2$}(NO)(PR$_3$)$_2$] (R = Cy **8a**, *i*Pr **8b**). **8a** and **8b** were isolated from the reaction mixture at 50−75 °C as deep green powders in 86% and 78% yield, respectively. The IR spectra of **8a** and **8b** displayed strong ν(NO) absorptions at 1646 (**8a**) and 1659 cm^{-1} (**8b**). In the ^{31}P{^{1}H} NMR spectra singlets were observed at 13.33 ppm (**8a**) and 22.80 ppm (**8b**), while in the ^{1}H NMR spectra the butadienyl ligand exhibited resonances at δ 8.74 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz), 5.43 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz), 4.38 (s), 4.17 (s) for **8a**, and 8.49 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz), 5.42 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz), 4.38 (s), 4.13 (s) for **8b**, which were assigned to the Re-CH=, =CH−, and =CH$_2$ moieties, respectively. The proton−proton coupling constant of 13 Hz strongly supported the *E*-stereochemistry at the vinylic Re-CH=CH− double bond.[13]

The five-coordinate hydride complex **1a** or **1b** also reacted with diynes in a similar manner to that with enynes (Scheme 3). Treatment of **1a** or **1b** with 0.5 equiv of 1,7-octadiyne afforded in an instantaneous reaction at room temperature the alkyne-coordinated binuclear rhenium hydride complexes, with

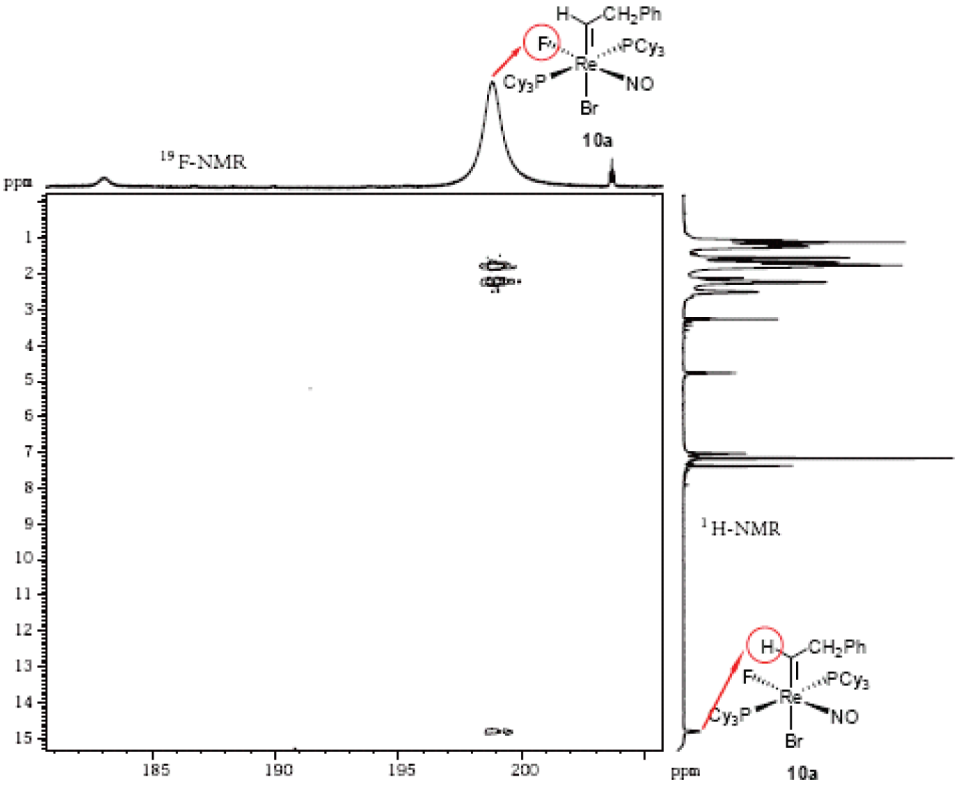
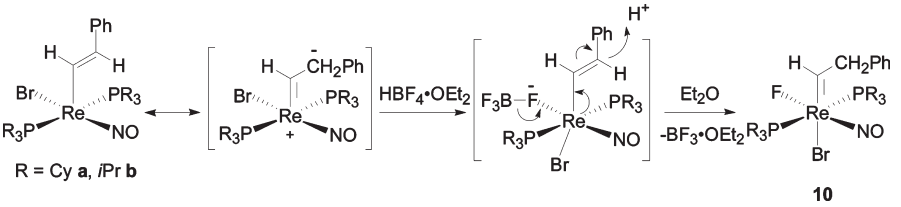


Figure 3. $^{19}F-^{1}H$-HOESY spectra of [Re(F)(Br)(=CHCH$_2$Ph)(NO)(PCy$_3$)$_2$] (**10a**) at 293 K in benzene-d_6.

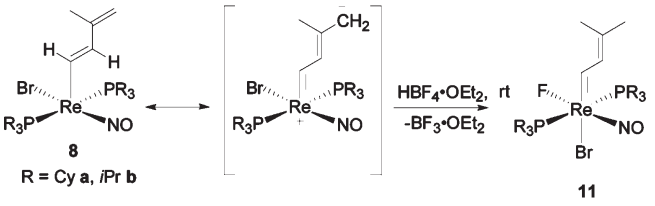
Scheme 5



strong evidence from the ^{31}P NMR spectra showing signals with unique AB patterns. The solutions were kept at 75 °C for 30 min, giving a deep green color. NMR spectroscopy indicated formation of the binuclear μ-bis-alkenyl derivatives [(PR$_3$)$_2$(NO)(Br)Re{(*E*)-CH=CH-(CH$_2$)$_4$-CH=CH-(*E*)}Re(Br)(NO)(PR$_3$)$_2$] (R = Cy **9a**, *i*Pr **9b**), which were isolated in 85% or 74% yield, respectively. The IR spectra showed strong ν(NO) absorptions at 1642 cm^{-1} for **9a** and 1638 cm^{-1} for **9b**. The $^{31}P\{^{1}H\}$ NMR spectra of **9a** revealed a singlet at δ 10.6 ppm, indicating the presence of chemically equivalent phosphines. In contrast the $^{31}P\{^{1}H\}$ NMR spectra of **9b** showed two signals with an AB coupling pattern at δ 21.6 (d, ^{2}J = 83 Hz) and 20.5 (d, ^{2}J = 83 Hz), indicating that the P*i*Pr$_3$ ligands are in slightly different chemical environment. We suppose the existence of *transoid* and *cisoid* conformational isomers with the rhenium centers either on the same or on opposite sides of the $-C_4H_8-$ chain and a slow exchange rate between them. In the ^{1}H NMR spectra a doublet at δ 7.64 ppm with a $J_{(HH)}$ coupling constant of 13 Hz and a multiplet at 4.26 ppm were attributed to the vinyl protons of **9a**. Similarly, a doublet at δ 7.41 ppm ($^{3}J_{(H\alpha H\beta)}$ = 13 Hz) and a multiplet at δ 4.25 ppm were assigned to the *E* vinylic protons of **9b**. In the $^{13}C\{^{1}H\}$ NMR spectra broad resonances at δ 135.4 and 135.7 ppm correspond to the C$_\alpha$(sp^2) atoms, and singlets at δ 130.6 and 131.6 ppm to the C$_\beta$(sp^2) atoms of **9a** and **9b**.

Deuterium labeling studies using [Re(Br)(D)(NO)(PCy$_3$)$_2$] and phenylacetylene were then carried out to support *syn* alkyne insertion into the Re−H bond. The reaction of [Re(Br)(D)(NO)(PCy$_3$)$_2$] exclusively furnished [Re(Br)((*Z*)-CH=CDPh)(NO)(PCy$_3$)$_2$] with the deuterium label at C$_\beta$ of the vinyl group. No evidence was provided for deuterium incorporation at the C$_\alpha$ atom. This result would indeed be consistent with a *syn* insertion stereochemistry of the alkyne. Addition of excess PCy$_3$ (10 equiv) at 75 °C did not influence the course of the η^2-alkyne (**2a**) to vinyl (**3a**) conversion. These results support the idea that the insertion proceeds with rearrangement of the coordination sphere from a geometry with the hydride *trans* to the acetylene ligand to one with the hydride *cis* to it, as depicted in Scheme 4. A similar mechanism was previously reported for the related ruthenium or osmium system [M(X)(H)(CO)(L)$_2$] (M = Ru and Os, L = PR$_3$). The alkyne coordinated *cis* to the hydride was calculated by DFT to be only 5 kcal mol^{-1} higher in energy than the *trans* η^2-alkyne.[7a] Furthermore, it is important to note that the conversion rates of the rhenium η^2-alkyne adducts to form the vinyl derivatives depends also on the type of phosphine ligand. The reaction rate of the P*i*Pr$_3$ derivative **1b** is generally higher than that of the PCy$_3$ compound **1a**. Any of the elementary steps of the proposed mechanism are

Scheme 6



facilitated with the sterically less hindered P*i*Pr$_3$ ligands. Finally, it should be mentioned that in contrast to the related Ru(II) and Os(II) hydrides, the described rhenium chemistry did not provide evidence for the appearance of vinylidene complexes.[6d]

Protonation of [Re(Br)((*Z*)-CH=CHR^1)(NO)(PR$_3$)$_2$] Complexes. Treatment of **3a** or **3b** with 1 equiv of $HBF_4 \cdot OEt_2$ in benzene solution afforded within 2 min at room temperature the new rhenium carbene species **10a**,**b**, which were isolated in 69% (**10a**) and 78% yield (**10b**) by extraction with Et_2O/hexane (1:10, v/v). The carbene complexes were identified as [Re(F)(Br)(=CHCH$_2$Ph)-(NO)(PR$_3$)$_2$] (R = Cy **10a**, *i*Pr **10b**), with the fluorine atom *cis* to the carbene ligand and the bromide *cis* to the NO ligand, established by various spectroscopic methods (Scheme 5). In the IR spectra of **10a** and **10b** strong ν(NO) absorptions at 1682 and 1673 cm^{-1} were found, appearing at significantly higher wavenumbers than the corresponding absorptions of the vinyl complexes. ^{1}H NMR multiplets at quite low field (δ 14.80 (**10a**) and 14.74 ppm (**10b**)) provide clear evidence for the presence of α-C*H* protons of carbene ligands. A multiplet resonance at δ 4.77 ppm for **10a** and a doublet at δ 4.54 (d, $^3J_{(HH)}$ = 8 Hz) ppm for **10b** were assigned to the methylene substituents of the carbene group. In the $^{13}C\{^1H\}$ NMR spectra a quartet at δ 298.2 ppm and a multiplet at 298.2 ppm were assigned to the $C_{carbene}$ atom of **10a** and **10b**, respectively. The quartet coupling pattern of the $C_{carbene}$ of **10a** arises from the coupling with the phosphorus and fluorine atoms with similar coupling constants (11.5 Hz), while for **10b** these coupling constants are apparently different, causing the multiplet structure. For both complexes we therefore assume that the F atom and the two phosphine ligands are located *cis* to the carbene ligand, which was further substantiated by a ^{19}F,^{1}H-HOESY experiment for **10a**, where dipolar F···H coupling (NOE) was detected, indicating spatial vicinity and the *cis* position of the F and the carbene ligands (Figure 3). The evolution of this geometry cannot be understood without rearrangement of the original vinyl coordination sphere, which stresses the geometrically flexible nature of such rhenium nitrosyl systems. One driving force for such a geometrical change could be the *trans* "push-pull" arrangement of the π donor fluoride and the π acceptor nitrosyl (Scheme 5). In the $^{31}P\{^1H\}$ NMR spectra fluorine-coupled doublets at δ 11.2 ppm (**10a**) and 24.2 ppm (**10b**) were observed. The magnitude of the $J_{(PF)}$ coupling constant (39 Hz) supported this further and excluded the presence of a Re-FBF$_3$ unit.[10a,18] In fact, $BF_3 \cdot OEt_2$ was detected as a byproduct originating from F−B cleavage, showing a singlet at δ −149 ppm in the $^{19}F\{^1H\}$ NMR spectra of the reaction solution.

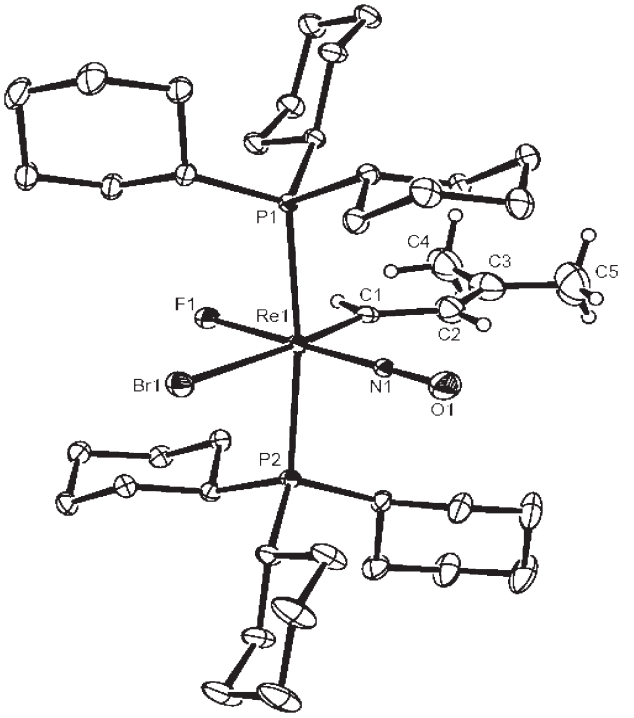


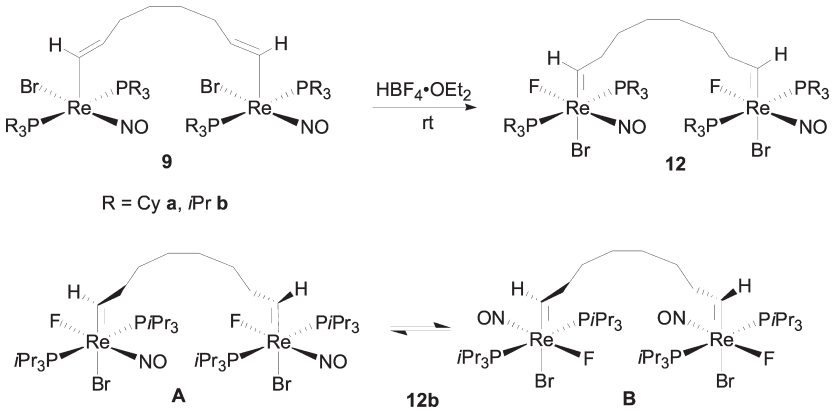
Figure 4. ORTEP drawing of [Re(F)(Br)(=CHCH=C-(CH$_3$)$_2$)(NO)(PCy$_3$)$_2$] (**11a**) with 30% probability ellipsoids. Selected bond lengths (Å): C(1)−Re(1), 1.949(3); C(1)−C(2), 1.412(4); C(2)−C(3), 1.366(4); N(1)−O(1), 1.188(2); N(1)−Re-(1), 1.7726(18); F(1)−Re(1), 1.9717(13); P(1)−Re(1), 2.5359(5); P(2)−Re(1), 2.5195(5); Br(1)−Re(1), 2.6740(3). Selected bond angles (deg): O(1)−N(1)−Re(1), 177.82(18); N(1)−Re(1)−F(1), 179.50(8); P(2)−Re(1)−P(1), 173.463(18); C(1)−Re(1)−Br(1), 172.34(8); C(2)−C(1)−Re(1), 133.2(2); C(3)−C(2)−C(1), 127.2(3).

In comparison to **3a** and **3b**, in which a large portion of the electron density resides on the β-carbon atom, the electron density of the butadienyl ligand of **8a** and **8b** can delocalize further onto the δ-carbon atom. Treatment of **8a** or **8b** with 1 equiv of $HBF_4 \cdot OEt_2$ at room temperature afforded in benzene solution the vinylcarbene complex [Re(Br)-(F)(=CHCH=C(CH$_3$)$_2$)(NO)(PR$_3$)$_2$] (R = Cy **11a**, *i*Pr **11b**) in 74% (**11a**) or 36% (**11b**) isolated yield, which established that protonation occurred at the δ-position of the butadienyl ligand (Scheme 6). The IR spectra showed a strong ν(NO) absorption at 1672 cm^{-1} (**11a**) and 1674 cm^{-1} (**11b**). The most prominent ^{1}H NMR feature of **11a** and **11b** concerns the multiplet structure of the resonance at δ 14.27 (**11a**) and the doublet of triplet structure of the resonance at δ 14.48 ppm ($^3J_{(HH)}$ = 13.8 Hz, $^3J_{(HP)}$ = 2.4 Hz) (**11b**), both of which were assigned to the Re=C*H*− protons. Doublet signals at δ 7.73 ($^3J_{(HH)}$ = 13 Hz, **11a**) and 7.98 ($^3J_{(HH)}$ = 13.8 Hz, **11b**) were assigned to the Re=CH−C*H*=CH− α-vinylene proton. As the most prominent feature in the $^{13}C\{^1H\}$ NMR spectra the $C_{carbene}$ atoms are attributed broad singlets at

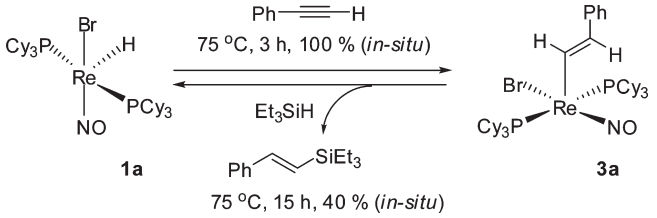
(17) X-ray crystal-structure data for **11a** (CCDC-730155): yellow crystals, $C_{53}H_{86}BrFNOP_2Re$, M = 1100.28, crystal size 0.35 × 0.24 × 0.14 mm^3, monoclinic, space group $P21/n$: a = 13.5086(1) Å, b = 21.8882(1) Å, c = 18.4925(1) Å, α = 90°, β = 107.488(1)°, γ = 90°, V = 5215.12(6) Å^3, Z = 4, ρ_{calcd} = 1.401 Mg·m^{-3}, $F(000)$ = 2272, μ = 3.197 mm^{-1}, 119 584 reflections ($2\theta_{max}$ = 61°), 15 921 unique (R_{int} = 0.0524), 508 parameters, $R_1(I > 2(I))$ = 0.0270, wR_2(all data) = 0.0622, GooF = 0.976, largest difference peak and hole 1.617 and −0.578 e·Å^{-3}.

(18) Berger, S.; Braun, S.; Kalinowski, H. O. *NMR Spectroscopy of the Non-metallic Elements*; John Wiley & Sons, Inc.: New York, 1996.

Scheme 7



Scheme 8



δ 275.0 (**11a**) or 273.6 (**11b**) ppm. The coordination sphere of **11a** and **11b** with chemically equivalent *trans* phosphorus ligands and the presence of a fluorine ligand is further substantiated through the appearance of doublets at δ 13.8 ppm (**11a**) and 23.8 ppm (**11b**) ($^2J_{(PF)} = 39$ Hz) in the $^{31}P\{^1H\}$ NMR spectra.

The molecular structure of **11a** was eventually fully established by a single-crystal X-ray diffraction study, as depicted in Figure 4 without the solvate molecule.[17] The rhenium atom can be ascribed a slightly distorted octahedron. The most noticeable feature is the fluorine atom F(1) disposed *cis* to the Re(1)−(C1) bond and the bromo atom Br(1) *cis* to the N(1)−O(1) ligand. The NO group is almost in line with the fluorine atom, with a N(1)−Re(1)−F(1) angle of 179.50(8)°. The phosphine ligands are disposed *trans* with a P(1)−Re(1)−P(2) angle of 173.463(18)°. The four atoms Re(1), C(1), C(2), and C(3) forming the butadienyl skeleton are in one plane. The Re(1)−C(1) bond distance of 1.949(3) Å and the C(2)−C(3) bond distance of 1.366(4) Å support the presence of Re(1)−C(1) and C(2)−C(3) double bonds.[19,16]

Treatment of the binuclear μ-bis-vinyl complexes $[(PR_3)_2(NO)(Br)Re\{(E)\text{-}CH{=}CH\text{-}(CH_2)_4\text{-}CH{=}CH\text{-}(E)\}\text{-}Re(Br)(NO)(PR_3)_2]$ (R = Cy **9a**, *i*Pr **9b**) with 2 equiv of $HBF_4 \cdot OEt_2$ in benzene solution at room temperature afforded the binuclear carbene derivatives $[(R_3P)_2(NO)(Br)(F)Re\{{=}CH\text{-}(CH_2)_6\text{-}CH{=}\}Re(F)(Br)(NO)(PR_3)_2]$ (R = Cy **12a**, *i*Pr **12b**), which were isolated in 55% (**12a**) and 82% (**12b**) yield (Scheme 7). The IR spectra showed strong ν(NO) absorptions at 1679 for **12a** and at 1674 cm^{-1} for **12b**, respectively, witnessing the presence of NO ligands. The $^{31}P\{^1H\}$ NMR spectra displayed a doublet at δ 13.1 ppm ($^2J = 39$ Hz) for **12a** and a signal with an AB pattern at 24.6 ($^2J = 39$ Hz), 19.1 ($^2J = 39$ Hz) ppm for **12b**, indicating that the two P*i*Pr$_3$ ligands are in different chemical environments. We assume that similar to the acetylene complexes the carbene ligand of **12b** possesses hindered rotation around the Re=C$_{carbene}$ bond with a preferred orientation of the carbene plane perpendicular to the P−Re−P axis. This is supposed to lead to the two rotational isomers **A** and **B** of **12b** given in Scheme 7. In the $^{13}C\{^1H\}$ NMR spectra the rhenium-bound C$_{carbene}$ atoms gave rise to broad signals at 301.3 ppm for **12a** and at 301.1 ppm for **12b**. In the ^1H NMR spectra the carbene ligands were assigned broad singlets at δ 14.76 (**12a**) and 14.58 (**12b**) ppm.

Finally, one interesting issue was pursued concerning the rhenium(I) vinyl derivatives: whether they could be recycled to the five-coordinated rhenium(I) hydrides **1**. In mechanistic studies on the osmium(II) hydride [Os(Cl)(H)(CO)(P*i*Pr$_3$)$_2$]-catalyzed hydrosilylation of phenylacetylene, it became apparent that the osmium vinyl compound [Os(Cl)((*Z*)-CH=CHPh)(CO)(P*i*Pr$_3$)$_2$] was inert toward further reaction with Et_3SiH.[5b] In contrast to this, we found that the rhenium(I) vinyl compound **3a** did react with Et_3SiH to afford the five-coordinated rhenium(I) hydride **1a** and the silyl-substituted olefins (Scheme 8). Treatment of the dark green benzene-d_6 solution of **3a** with 1 equiv of Et_3SiH at 75 °C led within 15 h to the formation of the rhenium(I) hydride compound **1a** in 40% spectroscopic yield (Scheme 8). ^1H NMR spectroscopy revealed that the (*E*)-PhCH=CH(SiEt$_3$) olefin was stereospecifically formed in the hydrosilylation process without any trace of the (*Z*)-PhCH=CH(SiEt$_3$) isomer. Despite this perfect selectivity, the catalytic activity of the rhenium(I) vinyl complex turned out to be poor, which prevented its application in catalytic hydrosilylations of alkynes with Et_3SiH. Indeed catalytic turnover was not observed for the reaction of phenylacetylene with Et_3SiH at 75 °C after 3 h in the presence of **1a** (2.0 mol %).

Conclusion

Five-coordinated 16-electron rhenium(I) hydride complexes [Re(Br)(H)(NO)(PR$_3$)$_2$] (R = Cy **1a**, *i*Pr **1b**) underwent terminal alkyne addition with subsequent insertion of the acetylenes into the Re−H bond, generating rhenium(I) vinyl species of the type [Re(Br)((*E*)-CH=CHR^1)(NO)(PR$_3$)$_2$]. The insertion rate is dependent on steric influences of the

(19) (a) Casey, C. P.; Strotman, N. A.; Guzei, I. A. *Organometallics* **2004**, *23*, 4121. (b) Casey, C. P.; Kraft, S.; Powell, D. R. *J. Am. Chem. Soc.* **2002**, *124*, 2584. (c) Bianchini, C.; Mantovani, N.; Marchi, A.; Marvelli, L.; Masi, D.; Peruzzini, M.; Rossi, R.; Romerosa, A. *Organometallics* **1999**, *18*, 4501. (d) Bianchini, C.; Marchi, A.; Marvelli, L.; Peruzzini, M.; Romerosa, A.; Rossi, R. *Organometallics* **1996**, *14*, 3203. (e) Bianchini, C.; Marchi, A.; Mantovani, N.; Marvelli, L.; Masi, D.; Peruzzini, M.; Romerosa, A.; Rossi, R. *Eur. J. Inorg. Chem.* **1998**, 211.

alkynes and the phosphine substituents. The rhenium(I) vinyl species could be converted into the six-coordinated 18-electron carbene derivatives $[Re(F)(Br)(=CHCH_2R^1)(NO)(PR_3)_2]$ applying $HBF_4 \cdot OEt_2$, in which the fluoride ligand is located *cis* to the carbene ligand and the bromide ligand *cis* to the nitrosyl group. This work not only revealed the reactive nature of the rhenium(I) hydride system to undergo facile insertions but also established a close analogy between the respective rhenium(I) nitrosyl and an isoelectronic ruthenium(II) or osmium(II) carbonyl chemistry. The insertion of acetylenes into the Re−H bond, as well as the established reductive elimination of silyl olefins from the vinyl complexes with silanes, would be part of a catalytic hydrosilylation cycle. However, attempts to achieve catalytic hydrosilylation turnovers did not meet with much success.

Experimental Section

General Procedures. All manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques or in a glovebox (M. Braun 150B-G-II) filled with dry nitrogen. Solvents were freshly distilled under N_2 by employing standard procedures and were degassed by freeze−thaw cycles prior to use. The deuterated solvent benzene-d_6 was dried with sodium/benzophenone and vacuum transferred for storage in Schlenk flasks fitted with Teflon valves. ^{1}H NMR, $^{13}C\{^1H\}$ NMR, and $^{31}P\{^1H\}$ NMR data were recorded on Varian Gemini-300, Varian Mercury 200, or Bruker DRX 500 spectrometers using 5 mm diameter NMR tubes equipped with Teflon valves, which allow degassing and further introduction of gases into the probe. Chemical shifts are expressed in parts per million (ppm). ^{1}H and $^{13}C\{^1H\}$ NMR spectra were referenced to the residual proton or ^{13}C resonances of the deuterated solvent. All chemical shifts for the $^{31}P\{^1H\}$ NMR data are reported downfield in ppm relative to external 85% H_3PO_4 at 0.0 ppm. Signal patterns are reported as follows: s, singlet; d, doublet; t, triplet; m, multiplet. IR spectra were obtained by using ATR methods with a Bio-Rad FTS-45 FTIR spectrometer. Microanalyses were carried out at the Anorganisch-Chemisches Institut of the University of Zurich. $[Re(Br)(H)(NO)(PR_3)_2]$ (R = Cy **1a**, *i*Pr **1b**) and $[Re(Br)(H)(NO)(PCy_3)_2]$ were prepared via previously reported procedures.[11,12] Phenylacetylene, (triethylsilyl)acetylene, 2-methyl-1-buten-3-yne, 1,7-octadiyne, and $HBF_4 \cdot OEt_2$ were purchased from Fluka and used without further purification. $[Re(Br)(D)(NO)(PCy_3)_2]$ was prepared from the reaction of $[ReBr_2(NO)(PCy_3)_2(\eta^2\text{-}H_2)]$ with Et_3SiD at 100 °C within 15 h.

[Re(Br)(H)(NO)(PCy$_3$)$_2$(η^2-HC≡CPh)] (2a). In a glovebox $[Re(Br)(H)(NO)(PCy_3)_2]$ (17.2 mg, 0.02 mmol) and phenylacetylene (3 μL, 0.025 mmol) were dissolved in a 20 mL vial in 2 mL of hexane. Immediately the violet solution turned light brown and a light yellow precipitate was formed. After 10 min the solvent was removed *in vacuo* and the residue was washed with hexane (1 × 1 mL) and dried again *in vacuo*, giving a light yellow powder. Yield: 18 mg, 95%. IR (ATR, cm^{-1}): ν(C−H) 2923, 2848, ν(NO) 1660. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 8.82 (d, $^3J_{(HP)}$ = 20 Hz, 1H, HC≡), 6.98−7.60 (m, 5H, Ph), 5.32 (t, $^2J_{(HP)}$ = 33.8, 34.2 Hz, 1H, Re−H), 1.25−2.72 (m, 66H, $P(C_6H_{11})_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 142.9, 125.6, 120.5, 106.9 (s, ≡*C*Ph), 106.8 (s, HC≡), 35.6 (s, P−C), 35.2 (s, P−C), 30.0 (t, *J* = 15 Hz, P−C), 27.8, 27.6, 26.8. $^{31}P\{^1H\}$ NMR (80.9 MHz, benzene-d_6, ppm): 13.9 (d, $^2J_{(PP)}$ = 112 Hz, 1P), 11.4 (d, $^2J_{(PP)}$ = 112 Hz, 1P). Anal. Calcd for $C_{44}H_{73}BrNOP_2Re$ (959.39): C, 55.04; H, 7.66; N, 1.46. Found: C, 55.50; H, 7.96; N, 1.36.

[Re(Br)(H)(NO)(P*i*Pr$_3$)$_2$(η^2-HC≡CPh)] (2b). In a glovebox $[Re(Br)(H)(NO)(PiPr_3)_2]$ (25.0 mg, 0.04 mmol) and phenylacetylene (5.6 μL, 0.05 mmol) were dissolved in a 20 mL vial in 2 mL of hexane. Immediately the violet solution turned light brown and a light yellow precipitate was formed. After 30 min the solvent was removed *in vacuo*, giving a light gray powder. Yield: 27 mg, 93%. IR (ATR, cm^{-1}): ν(C−H) 2961, 2870, ν(NO) 1661. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 8.78 (m, 1H, HC≡), 6.98−7.63 (m, 5H, Ph), 4.90 (t, $^2J_{(HP)}$ = 33.0, 33.8 Hz, 1H, Re−H), 2.70 (m, 6H, P−C*H*$(CH_3)_2$), 1.20 (m, 36H, P−CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 142.0, 125.6, 119.0, 106.1 (s, ≡*C*Ph), 106.0 (s, HC≡), 24.1 (m, P−*C*H$(CH_3)_2$), 18.9, 18.8, 18.7, 18.1. $^{31}P\{^1H\}$ NMR (80.9 MHz, benzene-d_6, ppm): 20.8 (s). Anal. Calcd for $C_{26}H_{49}BrNOP_2Re$ (719.20): C, 43.39; H, 6.86; N, 1.95. Found: C, 43.10; H, 7.01; N, 1.86.

[Re(Br)((*Z*)-CH=CHPh)(NO)(PCy$_3$)$_2$] (3a). In a 30 mL Young-tap Schlenk tube, $[Re(Br)(H)(NO)(PCy_3)_2]$ (96 mg, 0.11 mmol) and phenylacetylene (3 μL, 0.026 mmol) were dissolved in 3 mL of benzene. The violet solution turned immediately light green at room temperature. After stirring at 75 °C for 3 h, the solvent was evaporated *in vacuo*. The residue was washed with cold pentane (4 × 2 mL) and dried again *in vacuo*. Yield: 101 mg, 95%. IR (ATR, cm^{-1}): ν(C−H) 2929, 2850, ν(NO) 1648. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 9.47 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 1H, H_α), 6.77−7.39 (m, 5H, Ph), 5.50 (d, $^3J_{(H\alpha H\beta)}$ = 12 Hz, 1H, H_β), 1.19−2.75 (m, 66H, $P(C_6H_{11})_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 151.3 (C_α), 140.1, 130.2, 127.2, 125.0, 123.4 (C_β), 35.7 (t, $J_{(PC)}$ = 10 Hz, P−C), 30.2, 29.8, 27.8, 26.6. $^{31}P\{^1H\}$ NMR (80.9 MHz, benzene-d_6, ppm): 14.2 (s). Anal. Calcd for $C_{44}H_{73}BrNOP_2Re$ (960.12): C, 55.04; H, 7.66; N, 1.46. Found: C, 55.31; H, 7.65; N, 1.29.

[Re(Br)((*Z*)-CH=CHPh)(NO)(P*i*Pr$_3$)$_2$] (3b). In a 3 mL Young-tap NMR tube $[Re(Br)(H)(NO)(PiPr_3)_2]$ (24 mg, 0.04 mmol) and phenylacetylene (6 μL, 0.052 mmol) were dissolved in 0.5 mL of benzene-d_6. Immediately the violet solution turned light brown at room temperature. The solution was kept at 75 °C for 30 min, becoming deep green. The solvent was evaporated *in vacuo*, and the residue was washed with cold pentane (3×2 mL) and dried again *in vacuo*. Yield: 26 mg, 90%. IR (ATR, cm^{-1}): ν(C−H) 2962, 2929, 2872, ν(NO) 1643. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 9.21 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 1H, H_α), 6.78−7.31 (m, 5H, Ph), 5.46 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 1H, H_β), 2.70 (m, 6H, P−C*H*$(CH_3)_2$), 1.19 (m, 36H, P−CH(C*H*$_3$)$_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 151.1 (C_α), 139.7, 131.2, 124.9, 123.5 (C_β), 26.0 (t, $J_{(PC)}$ = 11 Hz, P−*C*H$(CH_3)_2$), 19.9, 19.7. $^{31}P\{^1H\}$ NMR (80.9 MHz, benzene-d_6, ppm): 29.8 (s). Anal. Calcd for $C_{26}H_{49}BrNOP_2Re$ (719.73): C, 43.39; H, 6.86; N, 1.95. Found: C, 43.17; H, 6.52; N, 1.73.

[Re(Br)((*Z*)-CH=CHSiEt$_3$)(NO)(PCy$_3$)$_2$] (5a). In a 3 mL Young-tap NMR tube $[Re(Br)(H)(NO)(PCy_3)_2]$ (35 mg, 0.04 mmol) and (triethylsilyl)acetylene (9 μL, 0.05 mmol) were dissolved in 0.5 mL of benzene-d_6. Immediately the violet solution turned light yellow at room temperature. After 2 h at room temperature the solution turned blue. The solution was kept at 75 °C for 30 min or at room temperature for 10 h, giving a deep blue solution. The solvent was removed *in vacuo*. The residue was washed with cold pentane (4×2 mL) and dried again *in vacuo*. Yield: 24 mg, 62%. IR (ATR, cm^{-1}): ν(C−H) 2925, 2850, 2872, ν(NO) 1648. ^{1}H NMR (300.1 MHz, benzene-d_6, ppm): 9.25 (d, $^3J_{(H\alpha H\beta)}$ = 14 Hz, 1H, H_α), 4.92 (d, $^3J_{(H\alpha H\beta)}$ = 14 Hz, 1H, H_β), 1.24−2.80 (m, 66H, $P(C_6H_{11})_3$), 1.21 (t, ^3J = 8 Hz, 9H, CH_3), 0.80 (q, ^3J = 8 Hz, 6H, $SiCH_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 169.5 (s, C_α), 125.8 (s, C_β), 35.6 (t, $J_{(PC)}$ = 10 Hz, P−C), 30.3 (s), 29.9 (s), 27.8 (m), 26.7 (s), 7.9 (s), 5.4 (s). $^{31}P\{^1H\}$ NMR (121.5 MHz, benzene-d_6, ppm): 13.4 (s). Anal. Calcd for $C_{44}H_{83}BrNOP_2ReSi$ (998.28): C, 52.94; H, 8.38; N, 1.40. Found: C, 52.62; H, 8.43; N, 1.34.

[Re(Br)((*Z*)-CH=CHSiEt$_3$)(NO)(P*i*Pr$_3$)$_2$] (5b). In a 3 mL Young-tap NMR tube $[Re(Br)(H)(NO)(PiPr_3)_2]$ (24 mg, 0.04 mmol) and (triethylsilyl)acetylene (8 μL, 0.044 mmol) were dissolved in 0.5 mL of benzene-d_6. Immediately the violet solution turned light purple at room temperature. After 15 h at room temperature the solution turned deep purple. The solvent was dried *in vacuo*. The residue was washed with cold

pentane (5×2 mL) and dried again *in vacuo*. Yield: 18 mg, 59%. IR (ATR, cm^{-1}): ν(C−H) 2958, 2932, 2908, 2872, ν(NO) 1642. ^{1}H NMR (300.1 MHz, benzene-d_6, ppm): 8.95 (d, $^3J_{(H\alpha H\beta)}$ = 14 Hz, 1H, H_α), 4.89 (d, $^3J_{(H\alpha H\beta)}$ = 14 Hz, 1H, H_β), 2.80 (m, 6H, P−C*H*$(CH_3)_2$), 1.20−1.30 (m, 36H, P−CH(C*H*$_3)_2$), 1.14 (t, $^3J_{(HH)}$ = 8 Hz, CH_3), 0.72 (q, $^3J_{(HH)}$ = 8 Hz, 6H, $SiCH_2$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, ppm): 170.2 (s, C_α), 126.9 (s, C_β), 25.5 (t, $J_{(PC)}$ = 10 Hz, P-*C*H$(CH_3)_2$), 19.8 (s), 8.1 (s), 5.5 (s). ^{31}P{^{1}H} NMR (121.5 MHz, benzene-d_6, ppm): 24.6 (s). Anal. Calcd for $C_{26}H_{59}BrNOP_2ReSi$ (757.90): C, 41.20; H, 7.85; N, 1.85. Found: C, 40.99; H, 7.58; N, 1.76.

Preparation of [Re(Br)((*Z*)-CH=CH$_2$)(NO)(PCy$_3$)$_2$] (7a) in Solution. In a 3 mL Young-tap NMR tube [Re(Br)(H)(NO)-$(PCy_3)_2(\eta^2$-$C_2H_2)$] (17.6 mg, 0.02 mmol) was dissolved in 0.5 mL of benzene-d_6. The compound is stable in solution at room temperature. After heating to 75 °C for 63 h, NMR spectroscopy indicated that the starting material was completely consumed with formation of **7a** in 56% yield along with two other unidentified species. The mixture could not be separated. **7a**: ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 8.60 (dd, $^3J_{(H\alpha H\beta)}$ = 10 Hz, $^3J_{(H\alpha H\gamma)}$ = 15 Hz 1H, H_α), 5.47 (d, $^3J_{(H\alpha H\beta)}$ = 10 Hz, 1H, H_β), 4.30 (d, $^3J_{(H\alpha H\gamma)}$ = 15 Hz, 1H, H_γ), 1.21−2.81 (m, 66H, P($C_6H_{11})_3$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, ppm): 151.7 (C_α), 115.5 (C_β), 35.8 (t, $J_{(PC)}$ = 10 Hz, P−C), 30.3, 29.9, 27.9, 26.7. ^{31}P{^{1}H} NMR (80.9 MHz, benzene-d_6, ppm): 11.8 (s). Unidentified species: ^{31}P{^{1}H} NMR (80.9 MHz, benzene-d_6, ppm): 28.5 (s), 3.8 (s).

[Re(Br)((*Z*)-CH=CH$_2$)(NO)(P*i*Pr$_3$)$_2$] (7b). In a 3 mL Young-tap NMR tube [Re(Br)(H)(NO)(P*i*Pr$_3)_2(\eta^2$-$C_2H_2)$] (26 mg, 0.04 mmol) was dissolved in 0.5 mL of benzene-d_6. The compound is stable in solution at room temperature. After heating at 75 °C for 15 h the solution turned deep blue. ^{1}H and ^{31}P NMR spectroscopy indicated that the starting material was completely consumed with the formation of **7b** in 92% yield (along with traces of free P*i*Pr$_3$). The solvent was evaporated *in vacuo*. The residue was washed with cold pentane (2×2 mL) and dried again *in vacuo*. Yield: 22 mg, 86%. IR (ATR, cm^{-1}): ν(C−H) 2960, 2924, 2871, ν(NO) 1664. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 8.30 (t, $^3J_{(H\alpha H\beta)}$ = 11 Hz, $^3J_{(H\alpha H\gamma)}$ = 12 Hz 1H, H_α), 5.46 (br, 1H, H_β), 4.27 (br, 1H, H_γ), 2.78 (m, 6H, P−C*H*$(CH_3)_2$), 1.27 (m, 36H, P−CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, ppm): 151.0 (C_α), 116.3 (C_β), 25.6 (t, $J_{(PC)}$ = 11 Hz, P−*C*H$(CH_3)_2$), 19.7, 19.6. ^{31}P{^{1}H} NMR (80.9 MHz, benzene-d_6, ppm): 22.6 (s). Anal. Calcd for $C_{20}H_{45}BrNOP_2Re$ (643.17): C, 37.32; H, 7.05; N, 2.18. Found: 37.60; H, 7.15; N, 2.03.

[Re(Br){CH=CHC(CH$_3$)=CH$_2$}(NO)(PCy$_3$)$_2$] (8a). In a 3 mL Young-tap NMR tube [Re(Br)(H)(NO)$(PCy_3)_2$] (26 mg, 0.03 mmol) and 2-methyl-1-buten-3-yne (3 μL, 0.032 mmol) were dissolved in 0.5 mL of benzene-d_6. Immediately the violet solution turned light brown at room temperature. The solution was kept at 50 °C for 15 h, giving a deep green solution. The solvent was evaporated *in vacuo*. The residue was washed with cold hexane (1×2 mL) and dried again *in vacuo*. Yield: 24 mg, 86%. IR (ATR, cm^{-1}): ν(C−H) 2920, 2848, ν(NO) 1646. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 8.74 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 1H, H_α), 5.43 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 1H, H_β), 4.38 (s, 1H, =C*H*H), 4.17 (s, 1H, =CH*H*), 2.04 (s, 3H, CH_3), 1.23−2.75 (m, 66H, P($C_6H_{11})_3$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, ppm): 150.2 (s, C_α), 141.5 (s), 134.7 (s, $=CH_2$), 104.0 (s, C_β), 36.0 (t, $J_{(PC)}$ = 10 Hz, P−C), 30.5, 30.0, 28.1, 26.9, 20.7 (s, CH_3). ^{31}P{^{1}H} NMR (80.9 MHz, benzene-d_6, ppm): 13.3 (s). Anal. Calcd for $C_{41}H_{73}BrNOP_2Re$ (923.39): C, 53.29; H, 7.96; N, 1.52. Found: C, 53.12; H, 7.83; N, 1.71.

[Re(Br){CH=CHC(CH$_3$)=CH$_2$}(NO)(P*i*Pr$_3$)$_2$] (8b). In a 3 mL Young-tap NMR tube [Re(Br)(H)(NO)(P*i*Pr$_3)_2$] (24.8 mg, 0.04 mmol) and 2-methyl-1-buten-3-yne (7 μL, 0.07 mmol) were dissolved in 0.5 mL of benzene-d_6. Immediately the violet solution turned light green at room temperature. The solution was kept at 75 °C for 10 min, giving a deep green solution. The solvent was evaporated *in vacuo*. The residue was washed with cold hexane (1× 2 mL) and dried again *in vacuo*. Yield: 21 mg, 78%. IR (ATR, cm^{-1}): ν(C−H) 2957, 2925, 2871, ν(NO) 1659. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 8.49 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 1H, H_α), 5.42 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 1H, H_β), 4.38 (s, 1H, $=CH_2$), 4.13 (s, 1H, $=CH_2$), 2.73 (m, 6H, P−C*H*$(CH_3)_2$), 1.93 (s, 3H, CH_3), 1.07− 1.32 (m, 36H, P−CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, ppm): 150.2 (s, C_α), 141.4 (s), 135.5 (s, $=CH_2$), 104.3 (s, C_β), 25.7 (t, $J_{(PC)}$ = 11 Hz, P−*C*H$(CH_3)_2$), 20.2 (s, CH3), 19.7, 19.4. ^{31}P{^{1}H} NMR (80.9 MHz, benzene-d_6, ppm): 22.8 (s). Anal. Calcd for $C_{23}H_{49}BrNOP_2Re$ (683.20): C, 40.40; H, 7.22; N, 2.05. Found: C, 40.56; H, 7.31; N, 2.01.

[(PCy$_3$)$_2$(NO)(Br)Re{(*E*)-CH=CH-(CH$_2$)$_4$-CH=CH-(*E*)}-Re(Br)(NO)(PCy$_3$)$_2$] (9a). In a 3 mL Young-tap NMR tube [Re(Br)(H)(NO)$(PCy_3)_2$] (34.4 mg, 0.04 mmol) and 1,7-octadiyne (2.70 μL, 0.02 mmol) were dissolved in 0.5 mL of benzene-d_6. The solution was heated at 75 °C for 30 min, giving a deep green solution. ^{1}H and ^{31}P NMR spectroscopy indicated complete consumption of the starting materials. The solvent was evaporated *in vacuo*, and the residue was extracted with hexane (2×2 mL). The combined extracted solutions were evaporated *in vacuo*. Yield: 31 mg (85%). IR (ATR, cm^{-1}): ν(C−H) 2919, 2848, ν(NO) 1642. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 7.64 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 2H, Re-CH=), 4.26 (m, 2H, =CH−), 0.84−2.81 (m, 140H, CH_2 and P($C_6H_{11})_3$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, ppm): 135.4 (br, Re-CH=), 130.6 (s, =CH−), 36.0 (t, $J_{(PC)}$ = 9 Hz, P−C), 30.5 (s), 30.1 (s), 28.1 (s, CH_2), 27.0 (s, CH_2). ^{31}P{^{1}H} NMR (80.9 MHz, benzene-d_6, ppm): 10.6 (s). Anal. Calcd for $C_{80}H_{144}Br_2N_2O2P_4Re_2$ (1822.13): C, 52.73; H, 7.97; N, 1.54. Found: 52.62; H, 8.03; N, 1.50.

[(P*i*Pr$_3$)$_2$(NO)(Br)Re{(*E*)-}CH=CH-(CH$_2$)$_4$-CH=CH-(*E*)-Re(Br)(NO)(P*i*Pr$_3$)$_2$] (9b). In a 3 mL Young-tap NMR tube [Re(Br)(H)(NO)(P*i*Pr$_3)_2$] (25.0 mg, 0.04 mmol) and 1,7-octadiyne (2.70 μL, 0.02 mmol) were dissolved in 0.5 mL of benzene-d_6. The solution was heated to 75 °C for 30 min, giving a deep green solution. ^{1}H and ^{31}P NMR spectroscopy indicated complete consumption of the starting materials. The solvent was evaporated *in vacuo*, and the residue was extracted with hexane (4×2 mL). The extracted solution was brought to dryness *in vacuo*. Yield: 20 mg (74%). IR (ATR, cm^{-1}): ν(C−H) 2958, 2925, 2871, ν(NO) 1638. ^{1}H NMR (200.0 MHz, benzene-d_6, ppm): 7.41 (d, $^3J_{(H\alpha H\beta)}$ = 13 Hz, 2H, Re-CH=), 4.25 (m, 2H, =CH−), 2.83 (m, 12H, P−C*H*$(CH_3)_2$), 2.01 (m, 4H, CH_2), 1.60 (m, 4H, CH_2), 1.26 (m, 72H, P−CH(C*H*$_3)_2$). ^{13}C{^{1}H} NMR (75.5 MHz, benzene-d_6, ppm): 135.7 (br, Re-CH=), 131.6 (s, =CH−), 37.7 (s, CH_2), 33.0 (s, CH_2), 25.8 (t, J = 10 Hz, P-*C*H$(CH_3)_2$), 19.8, 19.7. ^{31}P{^{1}H} NMR (80.9 MHz, benzene-d_6, ppm): 21.6 (d, $^2J_{(PP)}$ = 83 Hz, 1P), 20.5 (d, $^2J_{(PP)}$ = 83 Hz, 1P). Anal. Calcd for $C_{44}H_{96}Br_2N_2O_2P_4Re_2$ (1341.36): C, 39.40; H, 7.21; N, 2.09. Found: C, 39.62; H, 7.38; N, 2.10.

[Re(F)(Br)(=CHCH$_2$Ph)(NO)(PCy$_3$)$_2$] (10a). In a 3 mL Young-tap NMR tube [Re(Br)((*Z*)-CH=CHPh)(NO)$(PCy_3)_2$] (38.4 mg, 0.04 mmol) and $HBF_4 \cdot OEt_2$ (1.6 μL, 0.04 mmol) in ether solution were mixed in 0.5 mL of benzene. The violet solution turned yellow within 1 min. The solvent was evaporated *in vacuo*, and the residue was extracted with 3 mL of Et_2O/ hexane (1:10) mixture solvent. The extracted bright yellow solution was evaporated to dryness *in vacuo*. Yield: 29 mg (69%). IR (ATR, cm^{-1}): ν(C−H) 2922, 2849, ν(NO) 1682. ^{1}H NMR (500.25 MHz, benzene-d_6, ppm): 14.80 (m, 1H, Re=CH−), 7.01−7.39 (m, 5H, Ph), 4.77 (m, 2H, C*H*$_2$Ph), 1.18−2.51 (m, 66H, P($C_6H_{11})_3$). ^{13}C{^{1}H} NMR (125.8 MHz, benzene-d_6, ppm): 298.2 (m, Re=CH−), 141.0 (s), 129.1 (s), 128.6 (s), 126.8 (s), 55.2 (s, *C*H$_2$Ph), 37.1 (br, P−C), 28.6, 27.4, 26.2. ^{31}P{^{1}H} NMR (202.5 MHz, benzene-d_6, ppm): 11.2 (d, $^2J_{(PF)}$ = 39 Hz, 2P). ^{19}F NMR (188.1 MHz, benzene-d_6, ppm): −198.8 (br). Anal. Calcd for $C_{44}H_{74}BBrF_4NOP_2Re$ (1047.93): C, 50.43; H, 7.12; N, 1.34. Found: C, 50.68; H, 7.02; N, 1.44.

[Re(F)(Br)(=CHCH$_2$Ph)(NO)(P*i*Pr$_3$)$_2$] (10b). In a 3 mL Young-tap NMR tube [Re(Br)((*Z*)-CH=CHPh)(NO)(P*i*Pr$_3)_2$] (22 mg, 0.03 mmol) and $HBF_4 \cdot OEt_2$ (4.0 μL, 0.03 mmol) in ether

solution were mixed in 0.5 mL of benzene. The violet solution turned yellow within 2 min. The solvent was removed *in vacuo*, and the residue was extracted with 3 mL of Et_2O/hexane (1:10) mixture solvent. The extracted brown solution was evaporated *in vacuo*. Yield: 19 mg (78%). IR (ATR, cm^{-1}): ν(C−H) 2960, 2927, 2876, ν(NO) 1673. ^1H NMR (200.0 MHz, benzene-d_6, ppm): 14.74 (m, $^3J_{(HH)} = 8$ Hz, 1H, Re=CH−), 6.99−7.18 (m, 5H, Ph), 4.54 (d, $^3J_{(HH)} = 8$ Hz, 2H, CH_2Ph), 2.45 (m, 6H, P−CH(CH$_3$)$_2$), 1.25 (m, 36H, P−CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 298.2 (m, Re=CH−), 139.8 (s), 129.0 (s), 128.7 (s), 126.7 (s), 54.7 (s, CH_2Ph), 27.1 (t, $J_{(PC)} = 11$ Hz, P−CH(CH$_3$)$_2$), 18.6 (s), 18.3 (s). $^{31}P\{^1H\}$ NMR (80.9 MHz, benzene-d_6, ppm): 24.3 (d, $^2J_{(PF)} = 39$ Hz, 2P). ^{19}F NMR (188.1 MHz, benzene-d_6, ppm): −200.1 (br). Anal. Calcd for $C_{26}H_{50}BBrF_4NOP_2Re$ (807.21): C, 38.67; H, 6.24; N, 1.73. Found: C, 38.53; H, 6.30; N, 1.79.

[Re(F)(Br){=CH−CH=C(CH$_3$)$_2$}(NO)(PCy$_3$)$_2$] (11a). In a 3 mL Young-tap NMR tube [Re(Br){CH=CHC(CH$_3$)=CH$_2$}-(NO)(PCy$_3$)$_2$] (36.8 mg, 0.02 mmol) and $HBF_4 \cdot OEt_2$ (5.4 μL, 0.04 mmol) in ether were dissolved in 0.5 mL of benzene. The deep green solution turned brown within 1 min. The solvent was evaporated *in vacuo*, and the residue was washed with Et_2O (3×3 mL). The yellow residue was again dried *in vacuo*. Yield: 30 mg (74%). IR (ATR, cm^{-1}): ν(C−H) 2922, 2849, ν(NO) 1672. ^1H NMR (200.0 MHz, THF-d_8, ppm): 14.27 (t, $^3J_{(HH)} = 13$ Hz, 1H, Re=CH−), 7.73 (d, $^3J_{(HH)} = 13$ Hz, 1H, −CH=C), 1.24−2.35 (m, 72H, =C(CH$_3$)$_2$ and P(C$_6$H$_{11}$)$_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, ppm): 275.0 (s, Re=CH−), 142.0 (s, =C(CH$_3$)$_2$), 129.3 (s, −CH=), 37.0 (t, $J_{(PC)} = 10$ Hz, P−C), 29.4 (s), 29.0 (s), 28.6 (m), 27.3 (s), 19.7 (s, =C(CH_3)$_2$). $^{31}P\{^1H\}$ NMR (80.9 MHz, THF-d_8, ppm): 13.8 (d, $^2J_{(PF)} = 39$ Hz, 2P). ^{19}F NMR (188.1 MHz, THF-d_8, ppm): −196.7 (br). Anal. Calcd for $C_{41}H_{74}BBrF_4NOP_2Re$ (1011.40): C, 48.66; H, 7.37; N, 1.38. Found: C, 48.81; H, 7.43; N, 1.32.

[Re(F)(Br){=CH−CH=C(CH$_3$)$_2$}(NO)(P*i*Pr$_3$)$_2$] (11b). In a 3 mL Young-tap NMR tube [Re(Br){CH=CHC(CH$_3$)=CH$_2$}-(NO)(P*i*Pr$_3$)$_2$] was prepared *in situ* by the reaction of [Re(Br)(H)(NO)(P*i*Pr$_3$)$_2$] (49.6 mg, 0.08 mmol) with 2-methyl-1-buten-3-yne (16 μL, 0.16 mmol) at 75 °C for 30 min. Then $HBF_4 \cdot OEt_2$ (2.7 μL, 0.02 mmol) was added in ether, and the deep green solution turned deep brown within 2 min. The solvent was evaporated *in vacuo*, and the residue was washed with Et_2O (3 × 3 mL). The yellow residue was dried *in vacuo*. Yield: 22 mg (36%). IR (ATR, cm^{-1}): ν(C−H) 2961, 2924, 2874, ν(NO) 1674. ^1H NMR (200.0 MHz, THF-d_8, ppm): 14.48 (dt, $^3J_{(HH)} = 13.8$ Hz, $J_{(HP)} = 2.4$ Hz, 1H, Re=CH−), 7.98 (d, $^3J_{(HH)} = 13.8$ Hz, 1H, −CH=C), 2.58 (m, 6H, P−CH(CH$_3$)$_2$), 1.21−1.41 (m, 42H, =C(CH$_3$)$_2$, P−CH(CH_3)$_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, THF-d_8, ppm): 273.6 (s, Re=CH−), 141.3.0 (s, =C-(CH$_3$)$_2$), 140.9 (s, −CH=), 26.1 (t, $J_{(PC)} = 11.3$ Hz, P−C), 18.8 (s), 18.5 (s, =C(CH_3)$_2$), 18.2 (s), 19.7. $^{31}P\{^1H\}$ NMR (80.9 MHz, THF-d_8, ppm): 23.8 (d, $^2J_{(PF)} = 39$ Hz, 2P). ^{19}F NMR (188.1 MHz, THF-d_8, ppm): −201.7 (br). Anal. Calcd for $C_{23}H_{50}BBrF_4NOP_2Re$ (771.21): C, 35.81; H, 6.53; N, 1.82. Found: C, 36.05; H, 6.71; N, 1.99.

[(PCy$_3$)$_2$(NO)(Br)(F)Re{=CH-(CH$_2$)$_6$-CH=}Re(F)(Br)-(NO)(PCy$_3$)$_2$] (12a). In a 3 mL Young-tap NMR tube [(PCy$_3$)$_2$(NO)(Br)Re{(*E*)-CH=CH-(CH$_2$)$_4$-CH=CH-(*E*)}Re-(Br)(NO)(PCy$_3$)$_2$] was prepared *in situ* from the reaction of [Re(Br)(H)(NO)(PCy$_3$)$_2$] (34.4 mg, 0.04 mmol) and 1,7-octadiyne (2.70 μL, 0.02 mmol) at 75 °C for 1 h. Then $HBF_4 \cdot OEt_2$ in ether (around 1.6 μL) was added dropwise until the color became deep brown. The solvent was removed *in vacuo*, and the residue was extracted with Et_2O/pentane (1:10, 3 × 3 mL). The yellow solution was again evaporated *in vacuo*. Yield: 22 mg (55%). IR (ATR, cm^{-1}): ν(C−H) 2921, 2848, ν(NO) 1679. ^1H NMR (200.0 MHz, benzene-d_6, ppm): 14.76 (br, 2H, Re=CH−), 1.26−2.57 (m, 144H, CH$_2$ and P(C$_6$H$_{11}$)$_3$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 301.3 (s, Re=CH−), 49.7 (s), 37.4 (br, P−C), 30.2 (s), 29.8 (s), 29.1 (s), 28.8 (s), 28.1 (s), 26.8 (s). $^{31}P\{^1H\}$ NMR (80.9 MHz, benzene-d_6, ppm): 13.1 (d, $^2J_{(PF)} = 39$ Hz, 4P). ^{19}F NMR (188.1 MHz, benzene-d_6, ppm): −194.5 (br). Anal. Calcd for $C_{80}H_{146}B_2Br_2F_8N_2O_2P_4Re_2$ (1996.79): C, 48.10; H, 7.37; N, 1.40. Found: C, 48.43; H, 7.61; N, 1.24.

[(P*i*Pr$_3$)$_2$(NO)(Br)(F)Re{=CH-(CH$_2$)$_6$-CH=}Re(F)(Br)-(NO)(P*i*Pr$_3$)$_2$] (12b). In a 3 mL Young-tap NMR tube [(P*i*Pr$_3$)$_2$(NO)(Br)Re{(*E*)-CH=CH-(CH$_2$)$_4$-CH=CH-(*E*)}Re-Br(NO)(P*i*Pr$_3$)$_2$] was prepared *in situ* by the reaction of [Re(Br)(H)(NO)(P*i*Pr$_3$)$_2$] (24.8 mg, 0.04 mmol) and 1,7-octadiyne (2.70 μL, 0.02 mmol) at 70 °C for 30 min. Then $HBF_4 \cdot OEt_2$ in ether (around 1.6 μL) was added dropwise until the color became deep brown. The solvent was evaporated *in vacuo*, and the residue was extracted with Et_2O/pentane (1:10, 3× 3 mL). The yellow solution was evaporated *in vacuo*. Yield: 25 mg (82%). IR (ATR, cm^{-1}): ν(C−H) 2961, 2924, 2872, ν(NO) 1674. ^1H NMR (200.0 MHz, benzene-d_6, ppm): 14.58 (br, 2H, Re=CH−), 2.95 (m, 4H, CH$_2$), 2.62 (m, 12H, P−CH(CH$_3$)$_2$), 1.07−1.44 (m, 76H, CH$_2$ and P−CH(CH_3)$_2$), 0.86 (m, 4H, CH$_2$). $^{13}C\{^1H\}$ NMR (75.5 MHz, benzene-d_6, ppm): 301.1 (br, Re=CH−), 49.5 (s), 30.4 (s), 29.5 (s), 27.6 (t, $J = 10.4$ Hz, P−C), 19.1 (s), 18.8. $^{31}P\{^1H\}$ NMR (80.9 MHz, benzene-d_6, ppm): 24.6 (d, $^2J_{(PF)} = 39$ Hz, 2P), 19.1 (d, $^2J_{(PF)} = 39$ Hz, 2P). ^{19}F NMR (188.1 MHz, benzene-d_6, ppm): −192.2 (br), −199.7 (br). Anal. Calcd for $C_{44}H_{98}B_2Br_2F_8N_2O_2P_4Re_2$ (1516.41): C, 34.84; H, 6.51; N, 1.85. Found: C, 35.06; H, 6.82; N, 2.01.

Deuterium Labeling Studies Using [Re(Br)(D)(NO)(PCy$_3$)$_2$]. In a 3 mL Young-tap NMR tube [Re(Br)(D)(NO)(PCy$_3$)$_2$] (17.5 mg, 0.02 mmol) and phenylacetylene (2.4 μL, 0.02 mmol) were mixed in 0.5 mL of benzene. The tube was kept at 75 °C for 30 min, giving a dark green solution. $^2H\{^1H\}$ spectra indicated the unique formation of [Re(Br)((*Z*)-CH=CDPh)(NO)(PCy$_3$)$_2$], showing only one resonance at δ 5.20 ppm.

Test for the Hypothesis of Alkyne Insertion Pathway via Phosphine Dissociation. In a 3 mL Young-tap NMR tube, [Re(Br)(H)(NO)(PCy$_3$)$_2$(η^2-HC≡CPh)] (9.6 mg, 0.01 mmol) and PCy$_3$ (28 mg, 0.1 mmol) were mixed in 0.5 mL of C_6D_6. The solution was kept at 75 °C for 30 min, resulting in a dark green solution. ^1H NMR spectroscopy indicated the formation of the vinyl complex [Re(Br)((*Z*)-CH=CHPh)(NO)-(PCy$_3$)$_2$] in over 99% spectroscopic yield, showing almost no suppression.

Reaction of [Re(Br)((*Z*)-CH=CHPh)(NO)(PCy$_3$)$_2$] (3a) with Et$_3$SiH. In a 3 mL Young-tap NMR tube [Re(Br)((*Z*)-CH=CHPh)(NO)(PCy$_3$)$_2$] (**3a**) (19.0 mg, 0.02 mmol) and Et$_3$SiH (2.9 μL, 0.02 mmol) were mixed in 0.5 mL of benzene-d_6. The tube was kept at 75 °C for 15 h, resulting in a dark blue solution. ^1H and ^{31}P NMR spectroscopy indicated the formation of the five-coordinate rhenium(I) hydride complex **1a** in 40% spectroscopic yield with 60% **3a** still remaining in solution. The formation of *trans*-PhCH=CH-(SiEt$_3$) was observed as the only hydrosilylation product, bearing a characteristic doublet resonance at 6.45 ppm ($^3J_{(HH)} = 20$ Hz).

Attempt of Catalytic Hydrosilylation of Phenylacetylene with Et$_3$SiH. In a 3 mL Young-tap NMR tube [Re(Br)(H)-(NO)(PCy$_3$)$_2$] (**1a**) (4.3 mg, 0.005 mmol), Et$_3$SiH (38 μL, 0.25 mmol), and phenylacetylene (35 μL, 0.25 mmol) were dissolved in 0.5 mL of benzene-d_6. The tube was kept at 75 °C for 3 h. ^1H NMR spectroscopy indicated that both substrates remained unchanged in solution. No hydrosilylation product was observed.

Acknowledgment. Support from the Swiss National Science Foundation, the European COST Programme, and the Funds of the University of Zurich are gratefully acknowledged.

Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org. CIF file giving crystallographic data and refinement details for **3a**, **5a**, and **11a** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-730153−730155. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44)1223/336033; e-mail, deposit@ccdc.cam.ac.uk).